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Determination of the Distribution of Polydimethyl Siloxane Segment Lengths at the Surface of Poly(dimethyl siloxane) Segmented Copolymers

by

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Determination of the Distribution of Polydimethylsiloxane Segment Lengths at the Surface of Poly(dimethylsiloxane urethane) Segmented Copolymers by Time-of-Flight SIMS

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Abstract

Time-of-flight secondary ion mass spectra were recorded from submonolayer thin films of aminopropyl end-capped poly(dimethylsiloxane) (PDMS), and from thick films (*ca.* 50 μm) of poly(dimethylsiloxane urethane) (PU-DMS) segmented copolymers. Ions detected and assigned to fragments in the low mass range ($m/z \leq 300$) provided structural information about the repeat units and the end groups. The high mass spectrum of the PDMS homopolymer yielded a series of ions assigned to Ag^+-cationized oligomers; this enabled determination of the molecular weight distribution in comparison with GPC measurement. In the high mass (m/z=800-3500) spectra of thick PU-DMS films the peak series was assigned to a simple fragmentation process. That process would yield ions where the intact PDMS segment is present; it therefore can be used to evaluate the PDMS segment length distribution at the surface of the copolymer. It was found that the distribution of PDMS segment lengths segregated at the surface of the thick film was almost identical to that in the bulk for PU-DMS with PDMS nominal molecular weight of *ca.* 1000 Dalton. These results allow the development of an analysis of ion structure and a stepwise procedure for evaluating the segment length distributions in the near surface region of siloxanes.

Introduction

Over the past fifteen years, the use of electron spectroscopy for chemical analysis (ESCA) and infrared techniques have made great strides in relating the difference between polymer surface composition and structure and bulk composition and structure.[1] Much has been learned about the role of synthetic structural design and processing variations, and the resulting surface structure and composition of polymers. For example, as materials to be used in application for minimal biological adhesion, poly(dimethylsiloxane urethane) (PU-DMS) segmented copolymers have attracted intensive study.[2-5] With angle-dependent ESCA, much work has been done on the analysis of the surface composition of PU-DMS. In particular, the surface composition was correlated with the length of polydimethylsiloxane (PDMS) soft segments,[3, 4] different polyurethane (PU) hard segments,[3, 4] chain extenders in hard segments,[3, 4] and processing conditions including annealing [3] and solvents.[4] These results were evaluated using a concentration-depth profile deconvolution program and continuous concentration-depth profiles of the hard segment were reported in the near surface region.[3,4] This yields a more intuitive understanding of the compositional features of PU-DMS copolymers. Each aforementioned case showed a PDMS-rich surface due to the incompatibility of the soft segment and hard segment, and the lower surface energy of the soft segment in the segmented copolymers.

However, a quantitative description of segment length distribution at the surface of a multicomponent polymer remains elusive. Since, fundamentally, polymers involve a distribution of chain lengths which yields the particular properties, it would be desirable to know whether, at the surface, the distribution of segment or chain lengths is different than in the bulk. It is known that shorter polymer chains or segment lengths have different surface energies[6-8] and different mechanical properties. Therefore, like composition, the surface structure can lead to properties different than that predicted simply by knowledge of the bulk structure.

Recently, Ho and Wynne [9] introduced a method to evaluate ESCA data for PU-DMS

copolymers with a volume structural model which yields an average molecular weight (MW) of PDMS segments between hard blocks (PU). Using a Gaussian cylindrical model, they calculated that the average MW of the soft segments at the surface of PU-DMS with nominal PDMS MW of ~1000 Dalton in the bulk is 1080 Dalton. This method does not yield MW distributions however.

A surface sensitive mass spectrometric technique is necessary to accomplish this. Secondary ion mass spectrometry (SIMS) has been emerging as a potential tool, particularly with new time-of-flight (ToF) detection technologies which are able to yield increased resolution, mass range and transmission. ToF-SIMS experiments have been successful in determining oligomeric ion distributions from samples prepared by submonolayer coverage thin film casting[10] and converting these to accurate molecular weight distributions for a variety of mostly lower molecular weight (<10K) polymers. The ability to generate these distributions is likely due to the preparation which overcomes polymer chain entanglement[11,12] in the solid, which would mediate against volatilization and ionization of a representative high molecular weight polymeric solid. Previous workers have speculated that the difficulty in generating oligomeric distributions from solid surfaces, rather than the thin film preparation, is due to intrachain hydrogen bonding, besides the effects of chain entanglement. Research directed by Benninghoven and Hercules has been fruitful in this area, such as applying ToF-SIMS to the characterization of polyurethanes,[13] polymethacrylates,[10] polyamides,[14] polysiloxanes,[15,16] polyglycols, perfluorinated polyethers,[17] polystyrenes,[18] and polyesters.[19]

ToF-SIMS has yet to provide the information about segment length distribution at the surface of a multicomponent polymer, particularly in the form of a thick film. The difficulties in accomplishing this are primarily due to: (a) lack of structurally well-defined copolymers; (b) charging effects at the surfaces upon ion beam perturbation;[20] (c) lack of cationizing ions; and (d) polymer chain entanglement, interchain and/or intrachain interactions in a polymer. In many cases, however, a complete charge compensation for the analysis of an insulating sample can be

attained in ToF-SIMS by flooding the surface with low energy (10 eV) electrons pulsed in between ion pulses.[21]

To pursue this challenging goal, we focused on PU-DMS polymers in the present work, as a continuation of our previous study on potential minimal biological adhesion materials.[2-4] To our benefit, the PU-DMS segmented copolymer used in this study has not only a well-defined structure, but also has less chain entanglement thanks to the dominant content of PDMS in the copolymer, thus providing an effective template for our investigation. A preliminary account of such work has been reported.[22]

Experimental

A. Sample preparation

Aminopropyl end-capped polydimethylsiloxane (provided by Dr. İ. Yilgör of Goldschmidt Chemical Corp.) with nominal molecular weight of *ca.* 1000 Dalton, denoted as PDMS (1K) hereafter, was dissolved in tetrahydrofuran (THF) to make a solution of *ca.* 1mg/mL. 1μL of the solution was deposited on 100 mm^2 (equivalent to 6.0×10^{14} monomers/cm^2) of a Ag substrate which had been cleaned by etching in 20% nitric acid.

Poly(dimethylsiloxane urethane) (PU-DMS) based on aminopropyl end-capped PDMS (1K) oligomers and isophorone diisocyanate (IPDI) was prepared.[2] The molecular weight of the PU-DMS copolymer was determined by gel permeation chromatography (GPC): M_w=16,700; M_n=12,000; and M_w/M_n=1.4.[2] A PU-DMS solution of 0.5% (wt) in THF was made and cast into clean aluminum weighing pans. After air-drying, the thickness of the film was estimated to be *ca.* 50 μm.

B. Instrumentation

Gel permeation chromatography (GPC) was carried out using three Waters Ultrastyragel columns (10^2, 10^3 and 10^5 Å) or two narrow-bore Phenogel columns (linear pore size, Phenomenex) in series maintained at 35 °C, equipped with a Waters 590 programmable HPLC

pump, a Waters 410 differential refractometer maintained at 40 °C, and a Waters 745 Data Module. Molecular weights are relative to monodisperse polystyrene standards (Waters). Tetrahydrofuran (THF) was used as the solvent in the system.[23,24]

The ToF-SIMS instrumentation used has been described in detail elsewhere.[25] Typical data acquisition time was 600 to 700 s for the submonolayer films on Ag, and 1200 to 1500 s for the thick films. Peak areas were measured with baseline correction using the Googly program.[26] The mass values were dead time-corrected, and the peak area was justified by taking into consideration the possible effect of multiple ions striking the detector simultaneously; a Poisson statistical correction algorithm previously developed for ToF detection was used.[27]

Results and Discussion

Prior to copolymer analysis, the PDMS (1K) oligomer used for synthesizing the copolymer was analyzed with ToF-SIMS. As described in the Experimental Section, silver was used as the substrate. The known high volatility of Ag in the SIMS ion emission process leads to the cationization of PDMS oligomers, thereby minimizing the fragmentation of PDMS molecules and making the detection of PDMS molecular ions practical.

Figure 1a shows the positive ToF-SIMS spectrum from the submonolayer thin film of PDMS (1K) in the range of m/z=0-300. The peaks in Figure 1a are typical fragments originating from aminopropyl end-capped PDMS. For example, the peak at m/z = 116 is diagnostic of aminopropyl end groups; peaks at m/z = 59, 73, 133, 147, 207 and 281 are characteristic of PDMS repeat units. These results are consistent with Dong's work on aminopropyl-terminated PDMS.[16] In her work, PDMS containing different end groups were investigated to determine the effect of the end groups on fragmentation; the end groups in PDMS were identified by analysis of low mass range spectra. Aminopropyl end-capped PDMS, in particular, was included to examine the effect of nitrogen-containing end groups on the fragmentation of PDMS.

Figure 2a shows the positive ToF-SIMS spectrum from the submonolayer thin film of

PDMS (1K) in the range of m/z=600-2,200. Four series of peaks are observed in Figure 2a, as further illustrated in the inset therein. The first three series are fragmentation products from two single bond cleavages in the PDMS polymer backbone, or further combined with or loss of one hydrogen, without being Ag^+-cationized. The fourth series marked with asterisks (*), with a 74 Dalton mass interval (PDMS repeat unit) between two neighboring peaks in the same series, is attributed to the PDMS oligomer cationized by Ag^+. In Dong's work[16] on aminopropyl end-capped PDMS, only two peak series were observed, including the peak series assigned to the PDMS oligomers cationized by Ag^+. We attribute this disparity to the different sources of aminopropyl end-capped PDMS and possibly different coverage levels of the sample preparations. The PDMS Dong used was from Gelest (Tullytown, PA). It has been shown that the PDMS we used is comprised of 72% aminopropyl end-capped and 28% 2-amino-1-methylethyl end-capped.[2] The high percentage of 2-amino-1-methylethyl end-capped PDMS increases the propensity for the fragmentation of PDMS oligomers.

The isotopic cluster for Ag^+-cationized PDMS oligomers (the peak series marked with asterisks in Figure 2a) was compared with the theoretical one (see Figure 3). The intensity distribution of the fourth series was used to obtain the molecular weight distribution, the number (M_n) and weight (M_w) average molecular weights as well as the polydispersity (M_w/M_n) of PDMS homopolymers. The relative abundance versus the number of the repeat unit of PDMS oligomers is plotted in Figure 4a. The subsequently calculated M_n is 1062.3, M_w 1159.0, and M_w/M_n 1.09.

In comparison, an indirect approach to evaluating polymer molecular weights–GPC measurement (relative to polystyrene standards) of PDMS (1K) was conducted. The resultant M_n is 1244, M_w 1533 and M_w/M_n 1.23. M_n and M_w values are slightly greater than those from ToF-SIMS measurement. This discrepancy has been observed for other polymers[28] and attributed to variation in fragmentation and ionization/desorption processes, combined with the ToF-SIMS detection, providing a bias for small masses and thus shifting the molecular weight

distribution toward lower masses. The M_w/M_n from GPC measurement is also noticeably greater than that measured from ToF-SIMS due to the inherent broadening effect in GPC measurements.[29]

As noted in the Introduction, thick polymer films suffer from surface charging effects, lack of cationizing ions, and chain entanglement in ToF-SIMS measurement. In addition, the molecular weight of the PU-DMS used in this work is well above 10,000 Dalton. Such high molecular weights typically deter molecular ion generation and detection. In any case, it is not our current intent to determine the molecular weight distribution of PU-DMS copolymers themselves, instead, we are interested in learning the distribution of PDMS segment lengths at the surface of thick PU-DMS films. In other words, it suffices to generate and detect large fragments in which the intact PDMS segments are contained; and from this to extract the distribution of PDMS segment lengths at the surface.

Figures 1b and 2b show the positive ToF-SIMS spectra from the thick PU-DMS film in the range of m/z=0-300 and 1000-2500. Comparing Figure 1b with Figures 1a, a remarkable resemblance is seen between the spectrum from the copolymer and that originating from pure PDMS. This is a strong indication that the PDMS segment compositionally dominates the surface of the thick PU-DMS film, an observation consistent with earlier ESCA results.[3] The peaks in Figure 2b are separated from each other by 74 Dalton. According to a "Simple Statistical Model" for chain scission,[10] stating that only main-chain scission occurs, the masses of all possible fragments formed by any two chain-cleavages along the PU-DMS copolymer backbone were calculated and compared to the mass values of the peaks in Figure 2b. Only those fragments having the structure represented in Scheme 1 agree with the series observed in Figure 2b. Based on the assigned fragment structure, the length distribution (relative intensities vs. m values) was constructed and shown in Figure 4b, from which it was calculated that M_n =1131.3, M_w=1172.4, and M_w/M_n=1.1, very close to those values of the pure PDMS (1K) prepolymers. This result suggests that the PDMS segment segregated at the surface of the PU-DMS

copolymer with PDMS nominal MW of *ca.* 1000 Dalton is basically identical to that in the bulk in terms of PDMS segment length distribution.

Conclusions

ToF-SIMS enabled determination of the molecular weight distribution of PDMS homopolymers. The determined molecular weights (M_n and M_w) and molecular weight distribution (M_w/M_n) are in fairly good agreement with those values determined from GPC measurement.

More importantly, ToF-SIMS allowed us to examine the distribution of PDMS segment lengths at the surface of the PU-DMS copolymer. It was observed that the distribution of PDMS segment lengths segregated at the surface was nearly identical to that in the bulk for the PU-DMS copolymer with PDMS nominal MW of *ca.* 1000 Dalton. This accomplishment opens up a door to study segment length distributions at the surface of other siloxane copolymers as a function of bulk segment length distribution and polymer processing.

In addition, by comparing the low mass (m/z=0-300) spectra from the submonolayer PDMS prepolymer film on Ag and the thick PU-DMS copolymer film on Al, it was noted that the PDMS segment compositionally dominated the surface of the thick PU-DMS film. This observation agrees well with earlier ESCA results.

Acknowledgments

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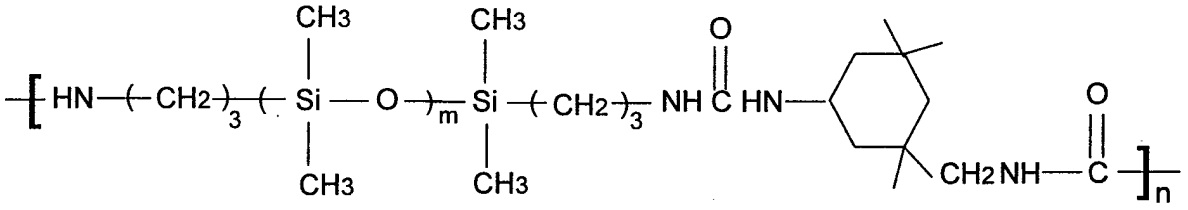
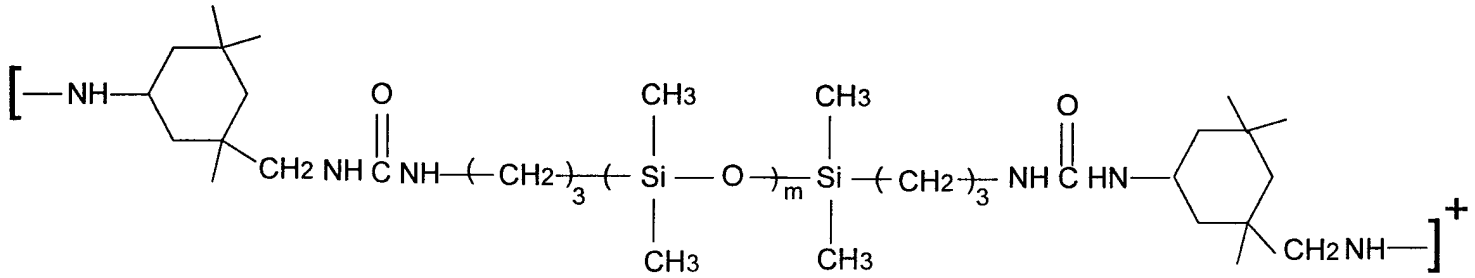
Scheme 1. Fragmentation mechanism of the PU-DMS copolymer in the form of a thick film.



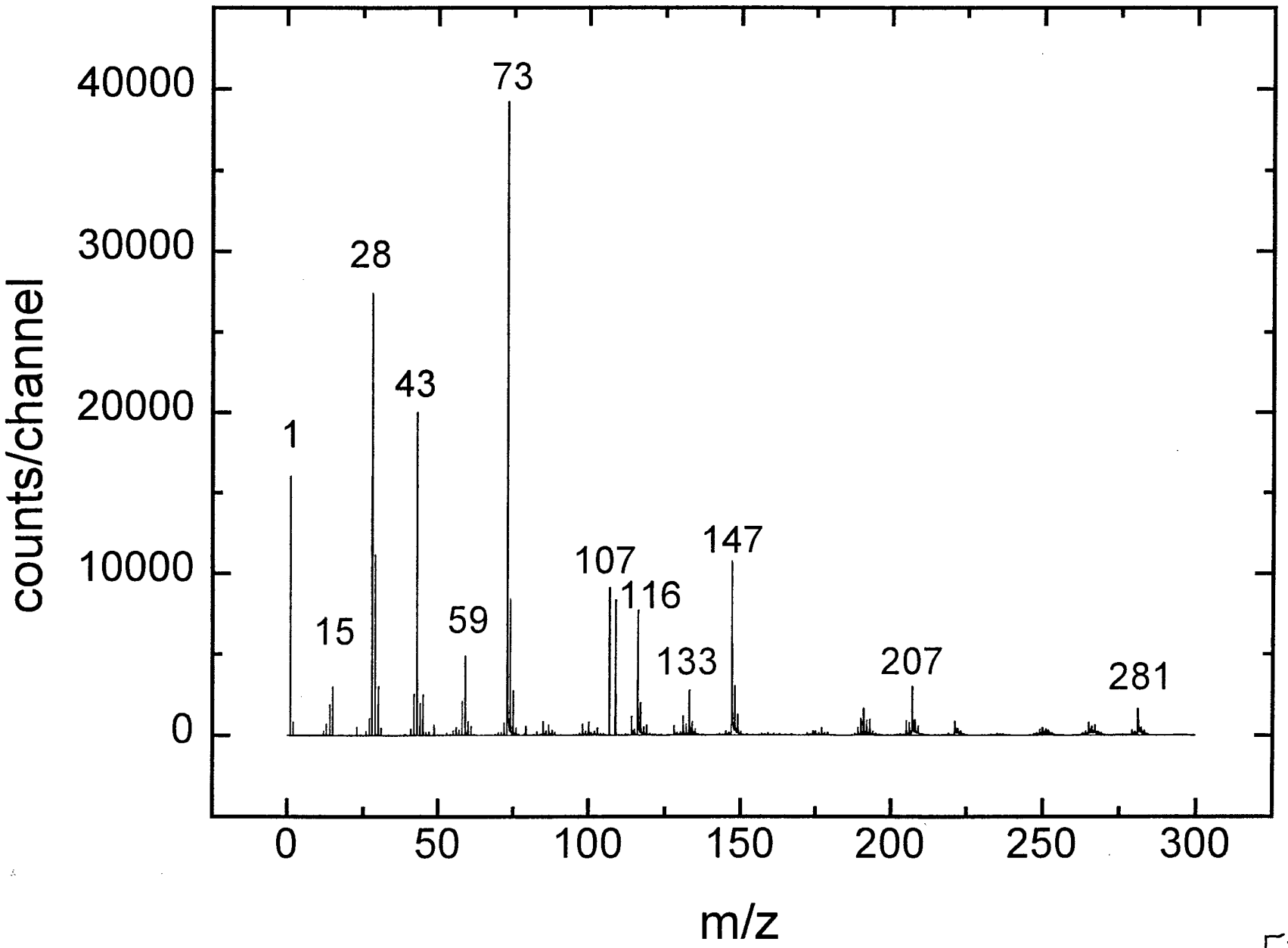
PU-DMS Copolymer

ion beam



Fragment

List of Figures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m/z

Fig. 1a

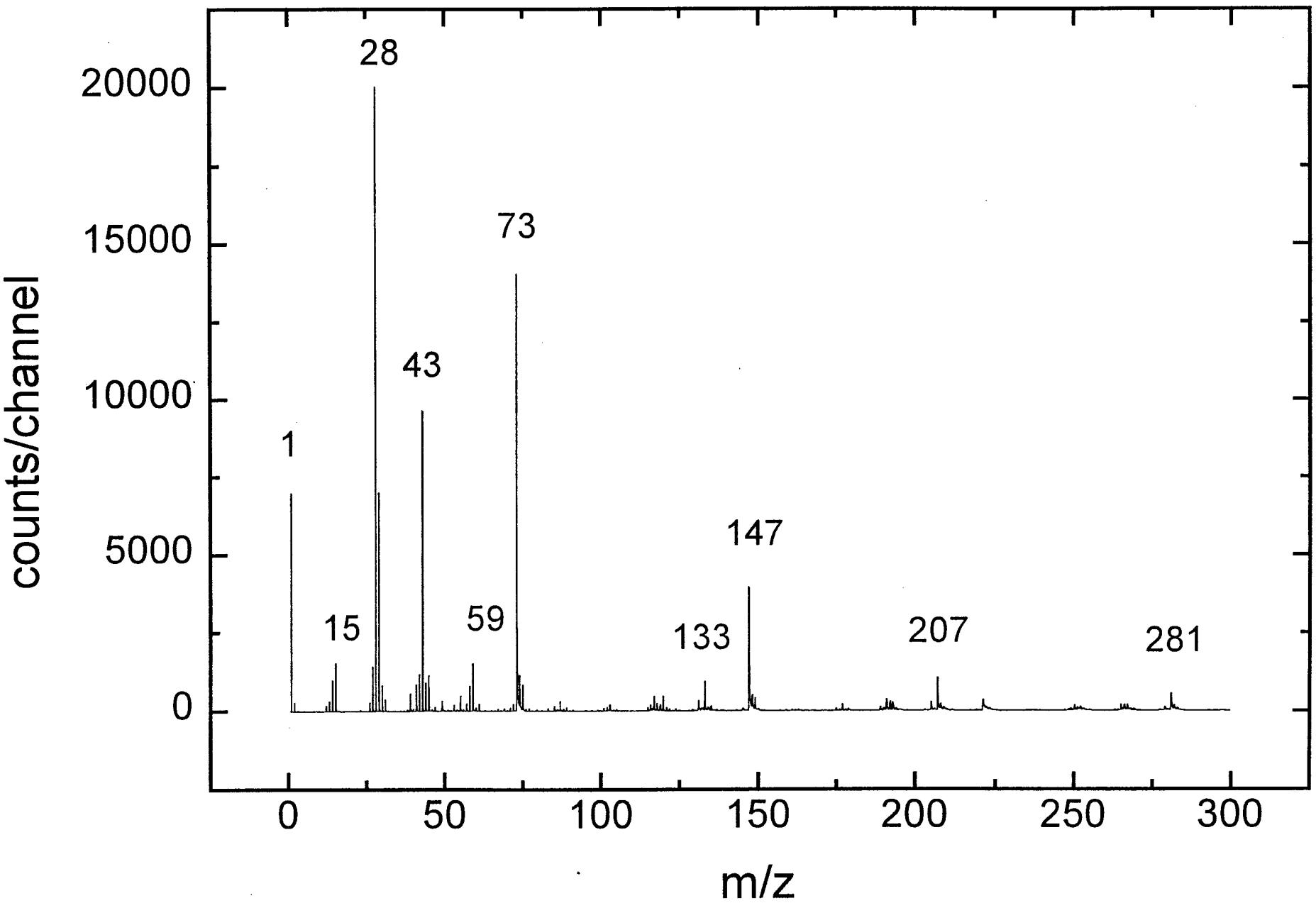
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Fig. 1b

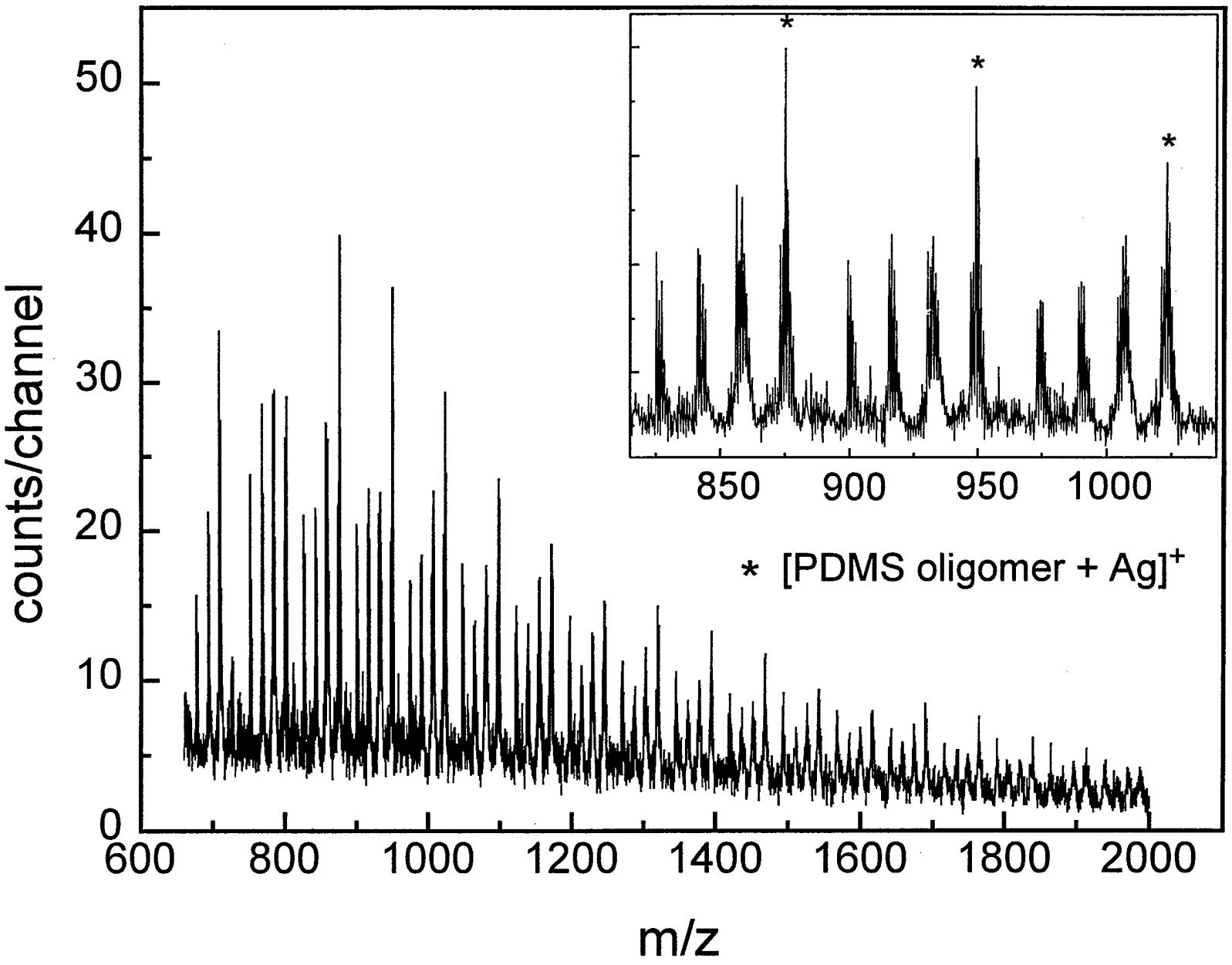
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Fig. 2a

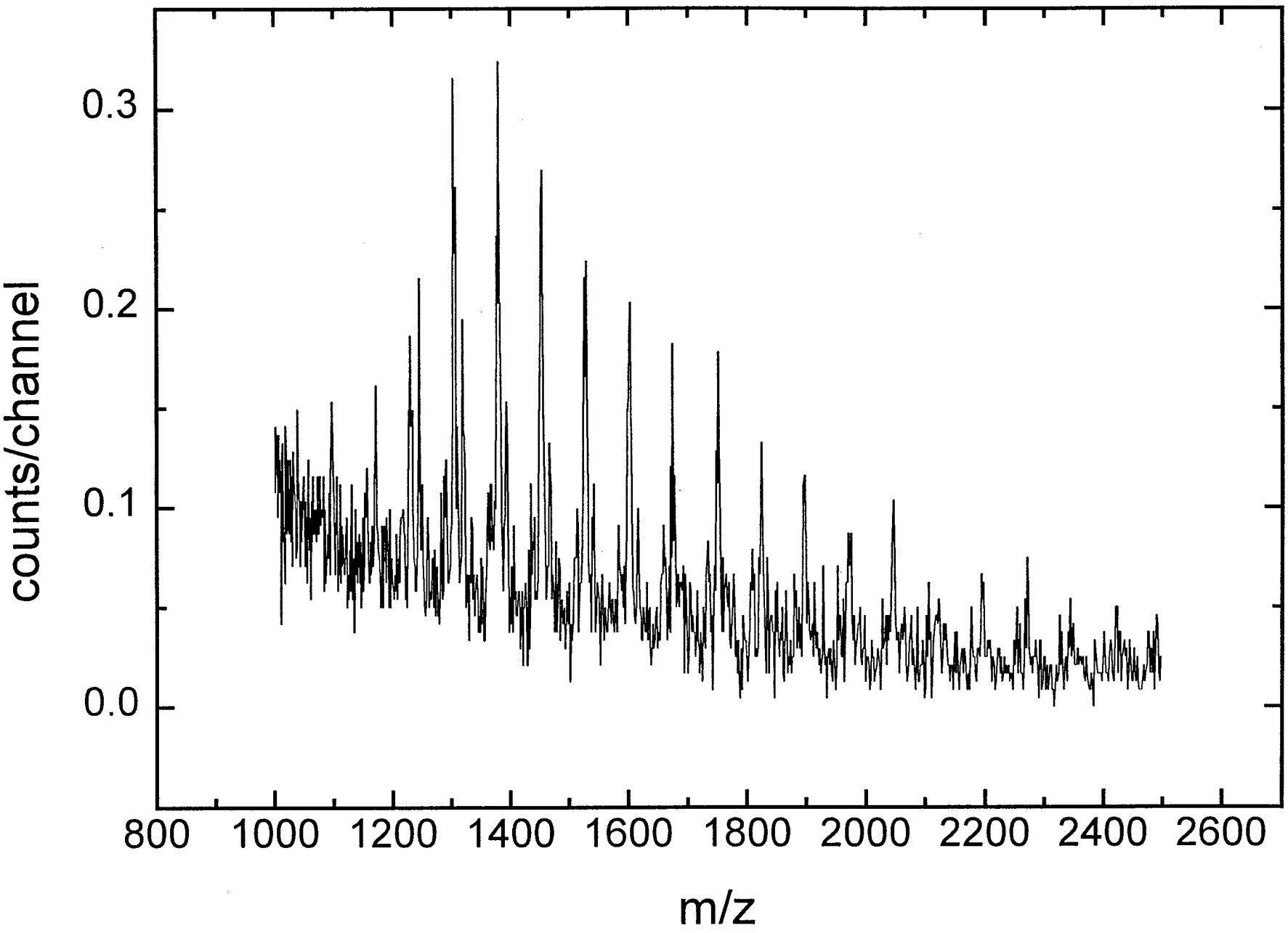
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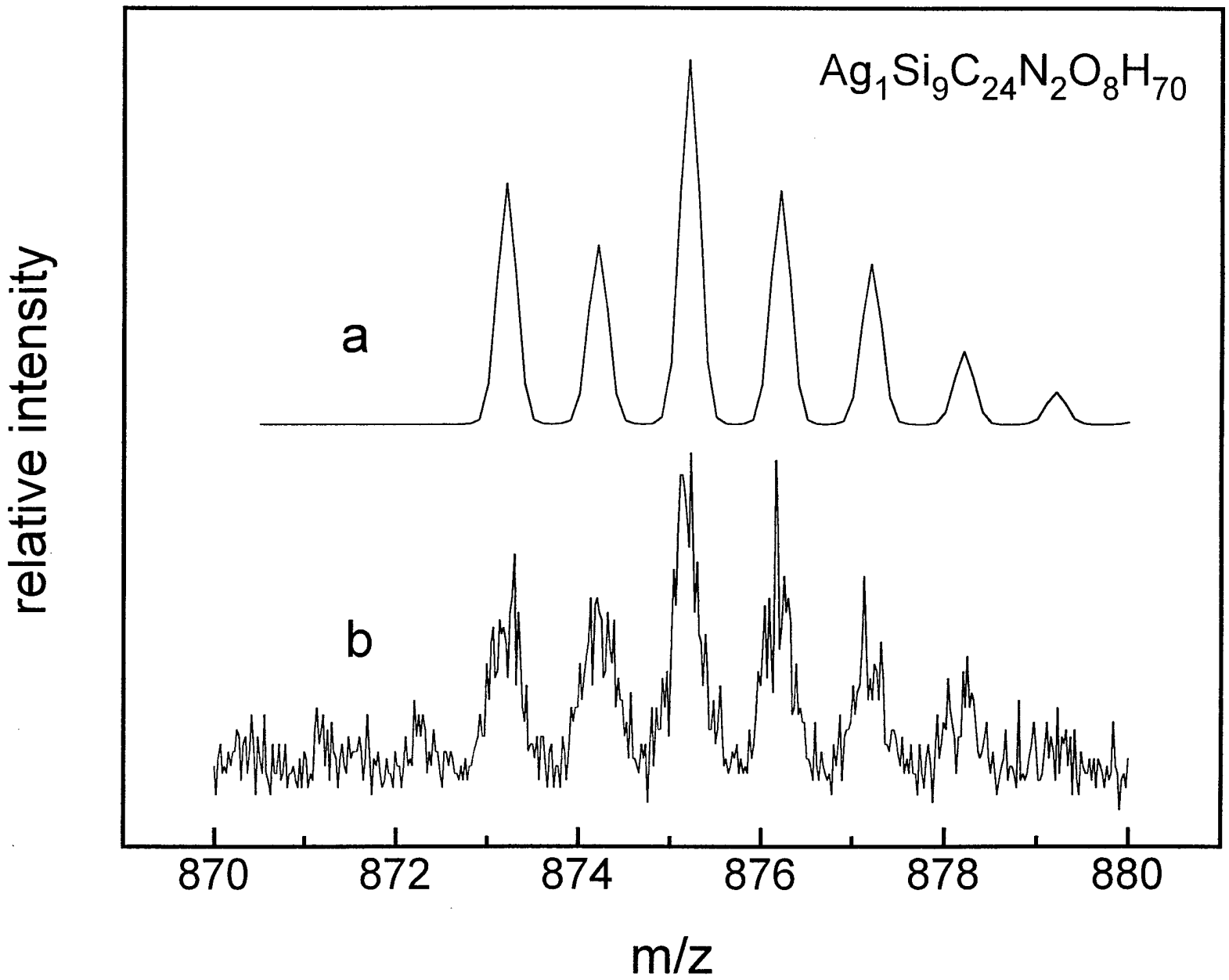
Fig. 2b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878
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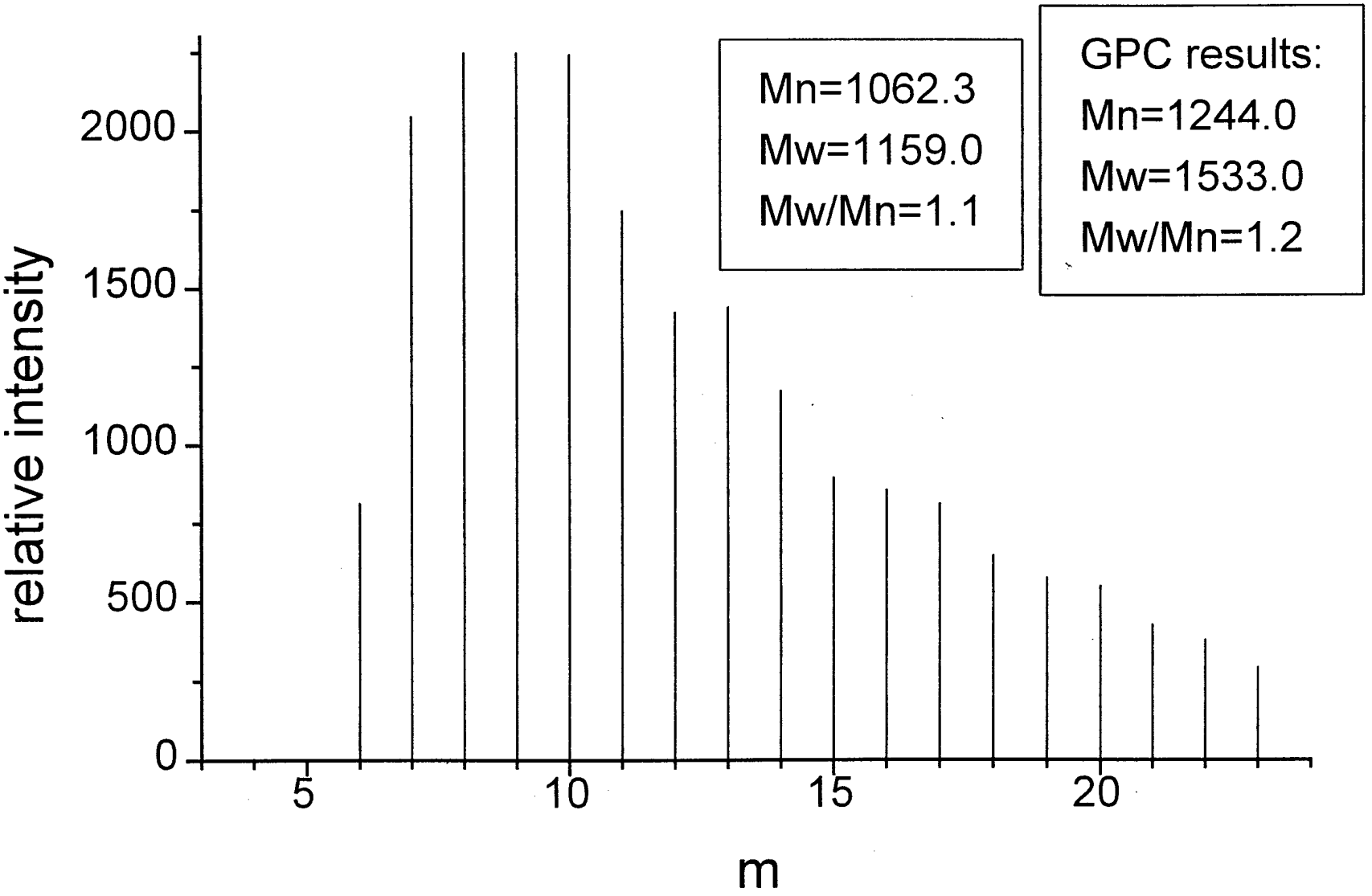
m/z

Fig. 3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Mw/Mn=1.1
GPC results:
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Mw/Mn=1.2
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15
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Fig.4a

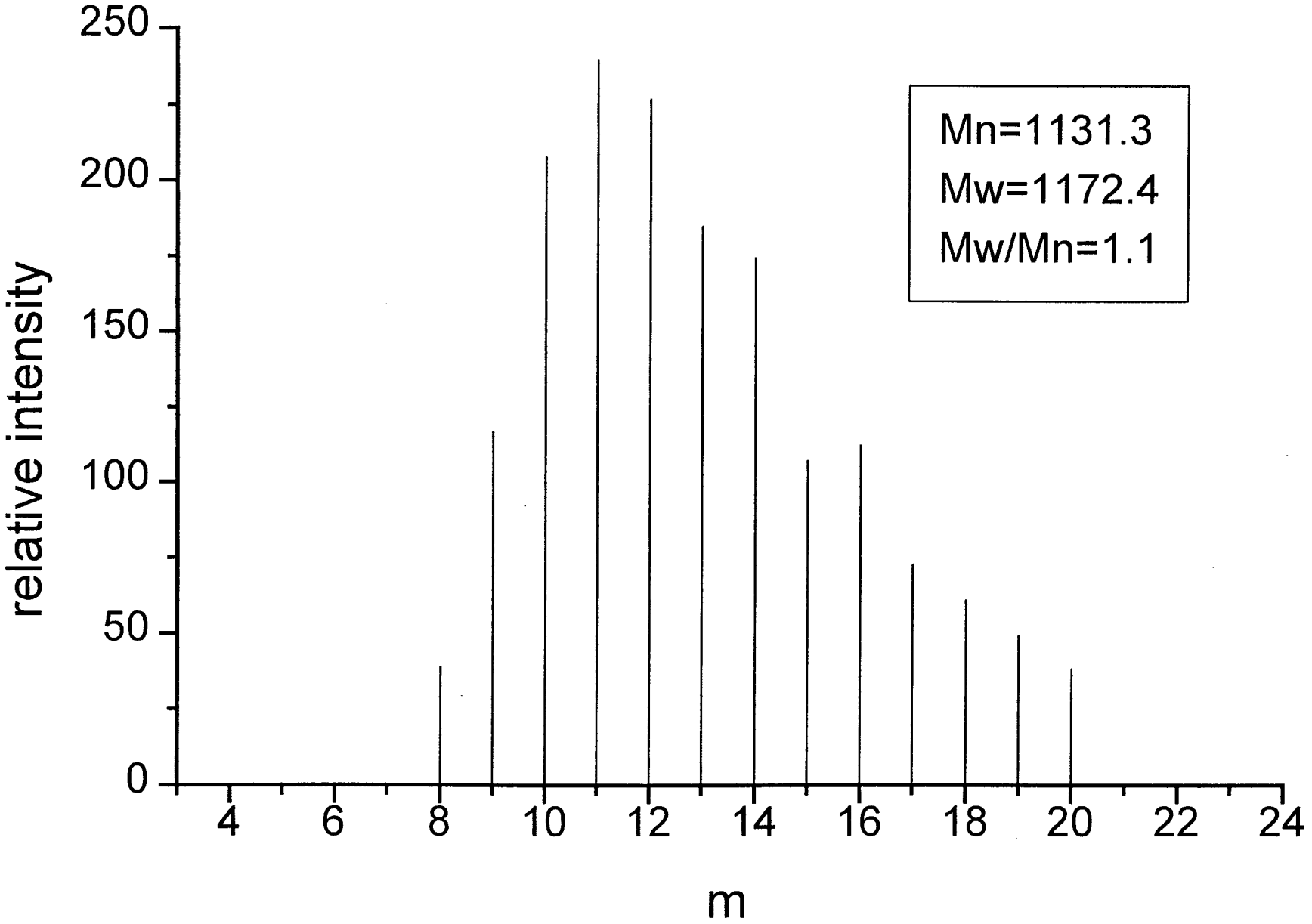
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Fig. 4b